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Short Communication

Dye-sensitized Solar Cell Based on N-Doped TiO_2 Electrodes Prepared on Titanium

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N-doped TiO_2 photoelectrodes were grown in situ on titanium sheet by micro-plasma oxidation method in electrolyte with $(NH_4)_2SO_4$ and $NH_3{\cdot}H_2O$ using as nitrogen sources, respectively. The photoelectric performance of the TiO_2 photoelectrode was studied by means of electrochemical impedance spectroscopy and *I-V* curves. The result shows that N-doping TiO_2 photoelectrode exhibits higher photoelectric performance than that of the pure TiO_2 photoelectrode. This property can be attributed to the synergetic effects of absorption in the visible-light region, red shift in adsorption edge and lower resistance of the N-doped TiO_2 photoelectrode.

Keywords: N-doped; TiO_2 photoelectrode; Titanium; Microplasma oxidation; Photoeletric performance

1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) have attracted extensive attention due to their low fabrication cost and relatively high efficiency. The photoelectric performance of DSSC is affected greatly by TiO_2 film electrode [1, 2]. Various methods of preparing TiO_2 film have been used [3-7]. However, most of these TiO_2 film electrodes are prepared by means of coating TiO_2 colloid on conductive glass and annealing at a high temperature, which is not fast and simple enough to produce the necessary devices with large area. So, simplifying preparation process is important for the practical application of DSSC.

Microplasma oxidation (MPO) method can sufficiently overcome the above-mentioned disadvantages [8]. MPO occurs at a potential above the breakdown voltage of the oxide films growing on the anode surface [9]. In this way, time and cost are reduced of producing TiO_2 thin films, and large areas of dye-sensitized solar cells are easily obtained to produce TiO_2 electrode. Moreover, the composition of the prepared film is easy to be changed through adding inorganic salts into the electrolyte [10, 11].

In this paper, MPO was used to prepare TiO_2 films on titanium substrates, and $NH_3 \cdot H_2O$ were doped into the electrolyte solution during the process of MPO. The objective of this research is to investigate the effect of doping N ions on the structural surface morphologies and photoelectric performances of the thin TiO_2 photoelectrode.

2. EXPERIMENTAL

2.1. Preparation of TiO_2 film

A titanium sheet washed in a HF-HNO_3 (1:1, V/V) aqueous solution was selected as an anode with a reaction area of 20 ×10 mm^2, and a copper sheet was introduced as a cathode. The TiO_2 film was prepared in 0.5 mol L^{-1} $(NH_4)_2SO_4$ solutions as electrolyte. $NH_3 \cdot H_2O$ was added into the above electrolyte to obtain the N-doped TiO_2 film. The N-doped TiO_2 prepared in different concentrations (2 ml L^{-1} M, 4 ml L^{-1}, 6 ml L^{-1}, 8 ml L^{-1} and 10 ml L^{-1}) of $NH_3 \cdot H_2O$ were respectively denoted by TN1, TN2, TN3, TN4 and TN5. The set-up scheme of the oxidation equipment is shown in previous work [10]. The MPO process was conducted on two stages for 10 min. First, a constant current density (14 $A \cdot dm^{-2}$) was performed, until a designated anode-to-cathode voltage (245 V) was reached. Then, the voltage was maintained before the oxidation ended.

2.2. Characterization of thin TiO_2 film

The surface morphology of the films was observed on a MX2600FE scanning electron microscope (SEM) from Cam Scan of England. The adhesion strength between Ti substrate and TiO_2 film in our paper was measured through scratch test. The X-ray diffraction (XRD) with a Cu Kα source (D/max-r B from Ricoh of Japan) was applied to studying crystalline structure of the films. The analysis of chemical states on X-ray photoelectron spectroscopy (XPS, ECSALAB 250, Thermo electron corporation, American) was performed with an Al kα source. The ultraviolet visible light diffuse reflectance spectra (UV-vis DRS) were measured with a Hitachi U3010 spectrophotometer.

2.3. Solar-cell assembly and photoelectrochemical characteristics

The prepared TiO_2 film was immersed in 0.3 mmol L^{-1} *cis-di*(thiocyanate)- *bis*(2,2-bipyridyl-4,4-dicarboxylate) ruthenium (II) in ethanol solution at room temperature for 24 h. The dye-coated TiO_2 film was used as working electrode, and transparent conducting glass (<20 □/Ω) as counter electrode. The electrolyte was a solution of 0.5 mol L^{-1} potassium iodide and 0.05 mol L^{-1} iodine in a mixture of ca. 80% acetonitrile and 20% glycol.

Electrochemical impedance spectroscopy (EIS) was measured on a Z263A impedance analyzer (Princeton Applied 125 Research, USA). The EIS was recorded beyond a frequency range of 0.01-10^5 Hz. The ac amplitude and the applied voltage were 10mV and set at open-circuit voltage of the cells, respectively. For the *I-V* curves measurements, the dye-sensitized TiO_2 films were illuminated through the conductive glass with an Xe lamp of 500-W high pressure with a water IR filter, and a 420 nm long pass UV filter as a light source in the place of the simulating sunlight.

3. RESULTS AND DISCUSSION

3.1. Characterization of mesoporous TiO_2 films

Fig.1 displays the SEM micrographs of titanium substrate (a), cross section of pure TiO_2 (b), pure TiO_2 (c) and TN3 (d). It can be seen that a uniform TiO_2 film has grown on the titanium surface, and the thickness of the film is about 10 μm. The surfaces of the prepared films are mesoporous. A comparison between Fig. 1(c and d) indicates that the pores size and the pore density of N-doped TiO_2 film pores increase more than that of pure TiO_2 film. In addition, the critical load of TiO_2 film was 35N.

3.2. Crystal structure

Fig. 2 illustrates the crystal structure of pure and N-doped TiO_2 films. The result indicates that all of the TiO_2 films consist of two phases, a large number of rutile and a small amounts of titanium. This means the addition of a small amount of N did not change the structure of TiO_2 film.

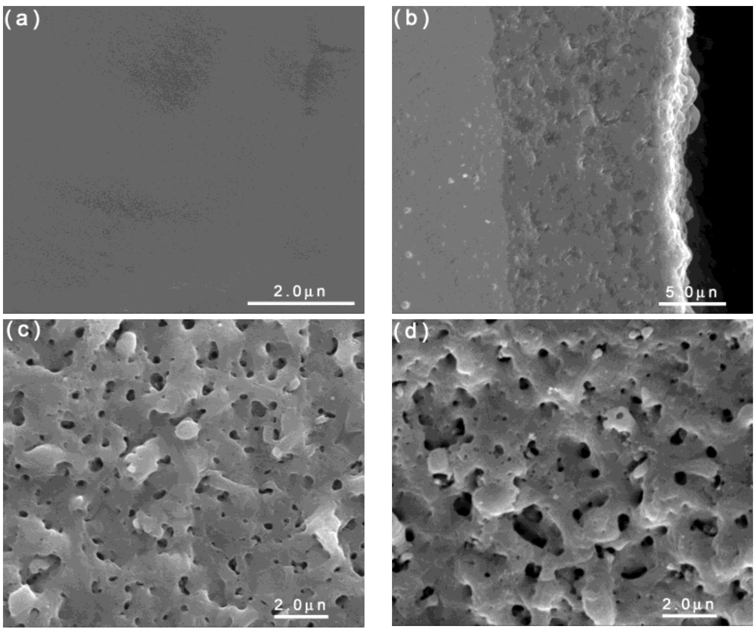

Figure 1. Microscope images of the samples: (a) titanium substrate; (b) cross section of pure TiO_2; (c) pure TiO_2; (d) TN3

But the diffraction peaks of (110) plane of the samples in the inset of Fig. 2 shows that the peak of (101) surface of N-doped film shifts slightly to a lower degree of 2θ. The crystal volumes of TN1, TN2, TN3, TN4 and TN5 are respectively 0.0626 0.0627, 0.0627, 0.0628, 0.0631 and 0.0629 nm^3 calculated by the Scherrer's formula, which suggests that the incorporation of nitrogen could enlarge the crystal particle. The shifts of (110) peaks indicate that the presence of lattice distortion which is probably caused by the incoming nitrogen.

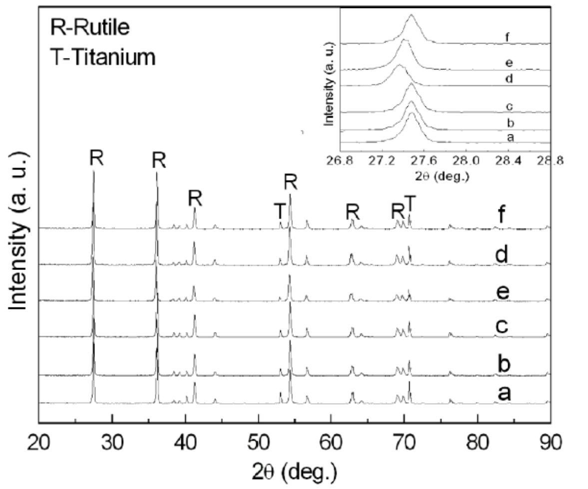

Figure 2. XRD spectrum of the TiO_2 films: (a) pure TiO_2; (b) TN1; (c) TN2; (d) TN3; (e) TN4; (f) TN5

3.3. XPS studies

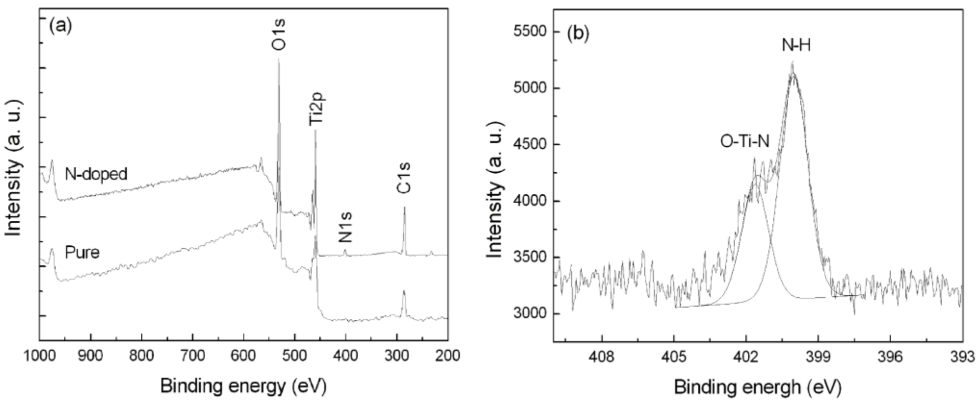

Figure 3. XPS spectrum of (a) TN3 and pure TiO_2; (b) N 1s levels for TN3

Fig. 3(a) shows the XPS spectrum of TN3. It can be noticed that both the pure TiO_2 and TN3 contain Ti, C, O, and a trace of N. The concentration of N increases when ammonia is added in the electrolyte. Fig. 3(b) also show that two nitrogen-containing species are incorporated into the as-prepared nitrogen-doped TiO_2. The peak at 401.6 eV is attributed to the substitutional O-Ti-N sites in the TiO_2 lattice. Another strong peak at 400.1 is assigned as molecularly chemisorbed γ N_2 (N-H). All of the above results prove that N is not only successfully implanted in the TiO_2 structure, but also has replaced the O^{2-} ions in the lattice of TiO_2. A lattice distort may be created due to different ionic radius between nitrogen and oxygen. XRD results justify the above deduction.

3.4. UV–vis DRS

The UV–vis absorption spectra of pure TiO_2 and N-doped TiO_2 samples prepared by the MPO are shown in Fig. 4. The band-gap of TiO_2 can be estimated from the intercept of UV-vis DRS of using the following equation: $Eg=1240/\lambda$. The absorption threshold of pure TiO_2 is 419.0 nm, which is corresponding to a band-gap of 2.96 eV. For TN2, TN3 and TN4, the band gap energies were respectively 2.880 eV, 2.863 eV and 2.873 eV, narrower than those of pure TiO_2. The maximum absorption of visible light was observed for TN3. It is demonstrated that N-doped TiO_2 can improve the absorption of visible light. The enhanced visible light absorption results from: (1) an isolated narrowband forms above the valance band of TiO_2 after nitrogen replacing oxygen [12]; (2) the nitrogen should be sat at a weak interaction site like an oxygen-deficient site. Several reports describe the subband-gap levels in their electron structures, which is responsible for the vis-activity [13, 14].

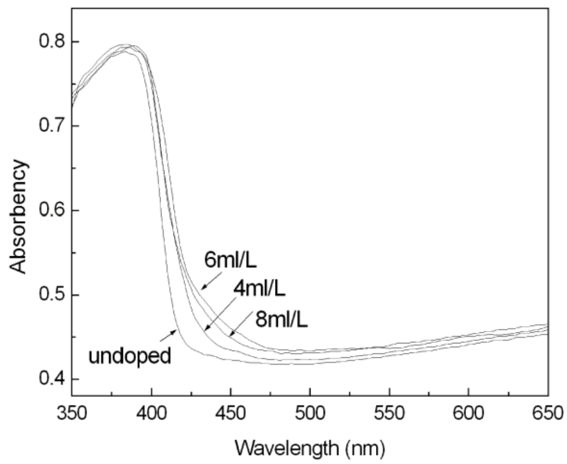

Figure 4. Figure UV–vis diffuse reflection spectroscopy of N-doped TiO_2 films

3.5. Electrochemistry characterization

Fig. 5 (a) shows the photo current–voltage (*J–V*) curve of the DSSC with pure and N-TiO_2 film. The short circuit current (J_{sc}) of the cell assembled with TiO_2, TN1, TN2, and TN3 increases from 149 to 165 μA · cm^2, while the open circuit voltage (V_{oc}) increases from 652 to 701 mV. When the cell is assembled with TN3, the $J_{sc,}$ and the V_{oc} reached maximum and then decreased at TN4 and TN5 respectively. The photoelectric transfer efficiency of the cell assembled with TN3 is 0.104%. These results indicate that the cells' performance is so sensitive that the appropriate nitrogen content should be demanded, which is almost nearly the same as other's report [15].

To study the effect of the N doping on the kinetics of electrochemical and photoelectrochemical processes occurring in DSSCs, EIS was conducted (see fig. 5 (b)). It can be noticed that every EIS shows one semicircle. The unique arc is attributed to the resistance of the charge-transfer process occurring at TiO_2/dye/electrolyte interface. This means that the charge-transfer resistances at the TiO_2 electrodes mainly affect the performance of DSSCs from these samples. The radius of the semicircles in Nyquist plot decrease after doping nitrogen into TiO_2. It is generally accepted that the less radius of the semicircle in Nyquist plots is, the slighter the electron recombination at the TiO_2/dye/electrolyte interface is. The comparison of these N-doped TiO_2 electrodes can result in the conclusion that the interfacial charge transfer resistance (R) of TN1, TN2, TN3, TN4 and TN5 decreases, and the impedance is lowest in TN3 compared with the pure TiO_2 electrode.

On the basis of impedance analysis of the DSSCs, we can conclude that a small quantity of N in TiO_2 significantly decreases surface resistance of TiO_2 electrode. Due to the decrease of resistance, electron is easy to be transferred to the underlying TiO_2, which results in the enhanced electron injection and increased conversion efficiency in DSSC. The arcs are the smallest, as the DSSC is assembled by TN3. This implies that the electron transfer between the counter electrode and electrolyte is the most successful. Therefore, the DSSC containing TN3 results in the highest photoelectric performance. Also, the plentiful pores on the surface of TN3 can improve the ability to absorb dye particles. This could make the higher *J*sc for the cell fabricated from N-doped TiO_2 electrode. Moreover, the TN3 exhibits a superior performance compared with the other TiO_2 electrodes, owing to the red shift of its absorption band which is propitious to sunlight absorption.

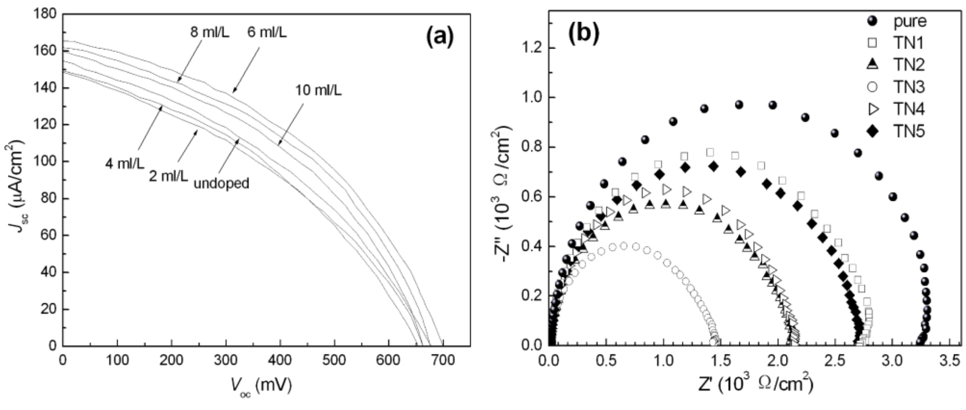

Figure 5. (a) *I-V* curve of cells prepared from different $NH_3 \cdot H_2O$ concentration; (b) Impedance spectra for TiO_2 and N-doped TiO_2 cells at open voltage

4. CONCLUSIONS

In conclusion, TiO_2 crystallite and pores are formed on the surface of the Ti substrate by MPO. N-TiO_2 films have been obtained by adding $NH_3 \cdot H_2O$ into the electrolyte. N-doping expands the crystal lattice, extends the absorbance spectra of TiO_2 into visible region and reduces the surface resistance of TiO_2 electrode, which leads to the improvement of the performance of solar cell based on N-doped TiO_2 films. In summary, MPO greatly shortens the preparation time. These advantages of MPO are of great effects on producing a large area dye sensitized solar cells in industry.

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